

Characterization of BCl_3/N_2 plasmas

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Optical emission spectroscopy, quadrupole mass spectrometry, and electron density measurements were used to study the effect of the percentage of N_2 on the characteristics of BCl_3/N_2 plasmas and their resulting etch processes. The etch rate of GaAs increased from 80 Å/min in pure BCl_3 to over 1000 Å/min in a 40:60 $\text{BCl}_3:\text{N}_2$ mixture (15 mTorr, 50 W, 20 sccm). The optical emission intensities of both molecular and atomic chlorine exhibited maxima near 30% N_2 , and an argon actinometer indicated a large increase in argon emission as a function of the increase in N_2 percentage. Microwave measurements indicated that the average electron density increased only slightly with an increase in nitrogen percentage up to 60% N_2 . Mass spectrometric analysis of the plasmas showed that both the dissociation of BCl_3 and the production of molecular chlorine were significantly enhanced by the addition of N_2 . These results suggest that an increase in the electron temperature as a result of electron attachment heating (and possibly energy transfer from N_2 metastables) is responsible for the increased dissociation and enhanced production of etch species. © 2003 American Institute of Physics. [DOI: 10.1063/1.1591075]

I. INTRODUCTION

Gas mixtures of boron trichloride and nitrogen have been used to etch a variety of materials. Howard and Steinbruchel reported the use of BCl_3/N_2 mixtures for the reactive ion etching of copper.¹ They found that the addition of nitrogen to BCl_3 plasmas resulted in considerably higher copper etch rates, and observed a maximum etch rate at 30% nitrogen. Their optical spectroscopy results showed that the addition of N_2 increased the atomic Cl emission. They also observed the presence of BN emission and suggested that the increased chlorine concentrations were due to the scavenging of boron by nitrogen to produce BN, thus preventing the recombination of atomic chlorine.

High etch rates for InGaP and InP were reported in electron cyclotron resonance (ECR) generated BCl_3/N_2 plasmas at 100 °C by Ren *et al.*² The maximum etch rate occurred at a composition of 25% nitrogen. Using optical emission spectroscopy, they found increases in the intensities of Cl and Cl_2^+ emission as well as the presence of BN emission. Shul *et al.* observed enhancement in the etch rates of GaAs, GaP, and GaN with the addition of N_2 to BCl_3 plasmas.^{3,4} Optimum etch rates were observed at 25% N_2 for GaAs and GaP in an ECR system,³ and at 40% N_2 for GaN in an inductively coupled plasma (ICP) system.⁴ Optical emission spectroscopy of the gas mixtures was performed and they found that their observations were in contradiction with those of Ren *et al.*² They were unable to identify BN emission or increased emissions for atomic or molecular chlorine.⁴ Fedison *et al.* have also used BCl_3/N_2 plasmas to reactively ion etch GaN.⁵ Their results indicated that the maximum etch rate of GaN occurred when 25% N_2 was added to BCl_3 plasmas.

A review of the literature on etch processes with BCl_3/N_2 plasmas reveals that there are still uncertainties as to the actual mechanism responsible for the enhanced chlorine production. Optical emission spectroscopy has been used to characterize this gas mixture but some data are contradictory. In this work we attempt to provide an in depth characterization of BCl_3/N_2 plasmas using optical emission spectroscopy (OES), quadrupole mass spectrometry (QMS), and microwave measurements of average electron densities.

II. EXPERIMENTAL PROCEDURE

The experiments described in this work were performed in a PlasmaTherm 790 parallel-plate reactive ion etch (RIE) system. The 10 in. diam aluminum powered electrode was operated at a frequency of 13.56 MHz. The upper electrode and chamber walls were grounded, and the top electrode was located approximately 3 in. above the powered electrode. The chamber was evacuated around the outer diameter of the powered electrode by a 150 l/s water-cooled turbo pump backed by a 32 cfm mechanical pump. Gases were introduced into the plasma chamber through a showerhead configuration in the top of the chamber, and were controlled by MKS mass flow controllers. Before etching, the chamber was evacuated to a base pressure of less than 1×10^{-5} Torr, and during etching the chamber pressure was kept constant with a throttle valve.

Etch studies were conducted on 1 cm×1 cm full thickness GaAs mechanical wafer pieces which were patterned with AZ4210 photoresist. Prior to loading the samples into the RIE chamber, they were baked on a hot plate at 90 °C for 1 min to enhance the etch resistance of the photoresist, then an oxide etch was performed in 1:30 solution of $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ for 15 s, followed by blow drying with nitrogen. Etched depths were measured with a DekTak surface

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profilometer after removal of the photoresist mask. The etch profile and morphology were examined using a scanning electron microscope (SEM).

The microwave measurement system used to monitor electron density consisted of a network analyzer (HP8722C) which was used to generate and detect the 32 GHz microwave signal. Details of the operating procedure are described elsewhere;⁶ only a brief description is provided here. The output from the network analyzer was coupled to a collimating antenna mounted flush to the Pyrex window of the plasma chamber with a high-quality radio-frequency (rf) cable. A similar antenna mounted at the other end of the chamber collected signals transmitted through the chamber. These signals are coupled to the network analyzer input port through another high-quality rf cable. The phase of the transmitted signal was measured with and without a plasma and the difference of these was used to obtain the phase shift experienced by the signal in propagating through the plasma. The line-averaged electron density was then calculated from this excess phase shift.⁷

Optical emission from the discharge was focused with a fused silica lens onto the slits of a Jobin-Yvon Spex Triax 550 spectrometer and detected with a Hamamatsu R928 photomultiplier. The entrance and exit slits of the spectrometer were 100 μm . The 750 nm argon emission line was chosen as an actinometer since it has been shown to be excited directly from the ground state and does not have a significant contribution from the argon metastable state.⁸

The 600 amu VG Quadrupoles SXP Elite mass spectrometry system was connected to the PlasmaTherm 790 reactor chamber via one of the viewports. Discharge species were sampled through a 100 μm diam orifice, and sampling pressures within the mass spectrometer were on the order of 10^{-7} Torr to reduce recombination reactions within the analyzer. The emission current of the spectrometer was set below 0.3 mA to minimize the effect of thermal dissociation of neutral species caused by hot electron emission from the filament. To insure that the mass signals originated only from neutrals in the plasma, and not from dissociative ionization within the mass spectrometer itself, appearance mass spectrometry was employed.⁹ This technique is based on the several electron volt energy difference between the appearance potentials for electron-impact ionization and the energy for dissociative ionization of parent molecules. For radicals such as BCl_2 , Cl_2 , and Cl the electron energy was set below the threshold appearance energy needed to observe the mass signal with the plasma off. An electron energy of 35 eV was used to monitor BCl_3 for dissociation measurements.

III. RESULTS AND DISCUSSION

The GaAs etch rate at 15 mTorr as a function of the percentage of N_2 in BCl_3/N_2 plasmas is shown in Fig. 1. The total flow and rf power were held constant at 20 sccm and 50 W, respectively. The corresponding dc bias is also shown. The etch rate increases from 80 $\text{\AA}/\text{min}$ in pure BCl_3 to 1070 $\text{\AA}/\text{min}$ at 60% N_2 . The bias voltage shows a slight increase with the addition of up to 80% N_2 , and it is possible that a small fraction of the etch rate enhancement observed is

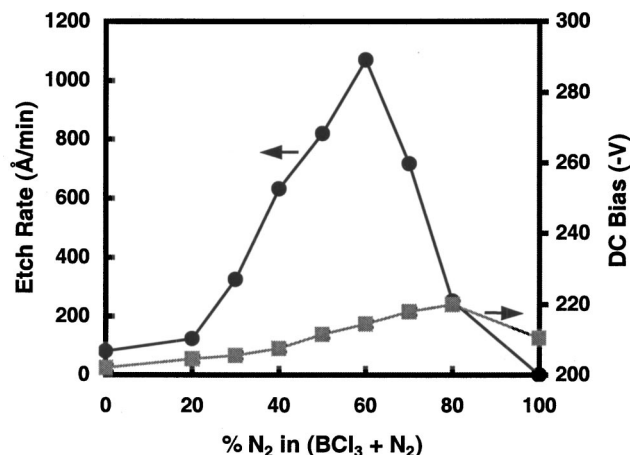


FIG. 1. Etch rate of GaAs in BCl_3/N_2 plasmas with the percentage of N_2 in the flow as a parameter (50 W, 15 mTorr, and 20 sccm). The dc bias voltage is also shown.

due to an increase in physical bombardment. SEM micrographs of a GaAs sample etched at 50 W and 60% N_2 are shown in Fig. 2. The etched surfaces are quite smooth and anisotropic. Some vertical striations are apparent on the sidewalls which are believed to be due to imperfections in the photoresist mask.

The optical emission intensities for atomic chlorine, molecular chlorine, and argon are shown in Fig. 3 as a function of the percentage of N_2 in the flow for a constant rf power of 50 W. The excited state emission from Cl and Cl_2^+ increases with an increase in N_2 and both exhibit maxima at approximately 30% N_2 . No evidence of BN emission was apparent. Argon was added to the gas mixture (2 sccm) as an actinometer, and its excited state emission increased significantly with the addition of N_2 . Since the ground state concentration of argon is constant (constant flow rate), the increase in its emission is an indication of a significant change in the electron density and/or the electron temperature.

The average electron density as a function of the applied rf power is shown in Fig. 4 for pure N_2 , pure BCl_3 , and a mixture of 50% N_2 in BCl_3 . The pressure and flow rate were held constant at 15 mTorr and 20 sccm, respectively. For each plasma, the electron density increases with an increase in the rf power applied, and the overall electron density in pure nitrogen is higher than for pure BCl_3 or the 50% N_2 mixture. At lower rf powers, the electron density of the 50% N_2 mixture is almost the same as that of the pure BCl_3

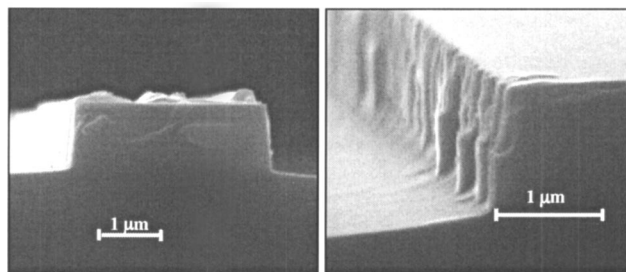


FIG. 2. SEM micrographs of GaAs etched with 60% N_2 in a BCl_3/N_2 plasma (15 mTorr, 50 W, 20 sccm, 5 min).

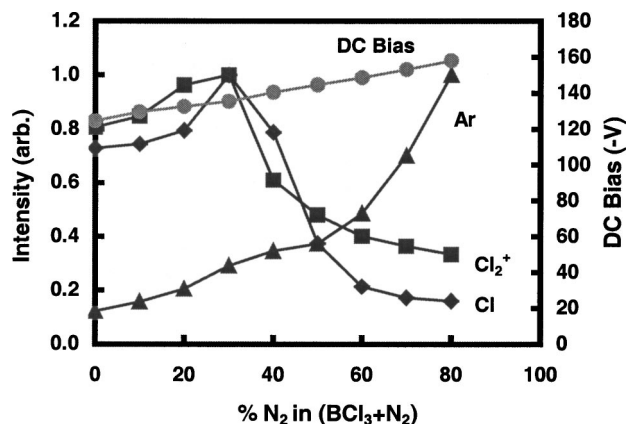


FIG. 3. Normalized optical emission intensities of Ar (750.4 nm), Cl_2^+ (396.2 nm), and Cl (792.5 nm) as a function of the percentage of N_2 in the flow for BCl_3/N_2 plasmas [50 mTorr, 50 W, 20 sccm ($\text{BCl}_3 + \text{N}_2$), 2 sccm Ar]. The dc bias is also shown.

plasma, and as the rf power increases, the 50% N_2 mixture has a slightly higher electron density than the pure BCl_3 plasma. The fact that the average electron density does not significantly increase with the addition of electropositive N_2 is an indication that electron attachment occurs.

The average electron density and dc bias voltage are shown as functions of nitrogen percentage in Fig. 5. The rf power, pressure, and total flow rate were held constant at 100 W, 15 mTorr, and 20 sccm, respectively. There was less than a 20% increase in the average electron density as the percentage of nitrogen was increased from 0% to 60%. From Fig. 1, over this same range of nitrogen (and only half the rf power), the etch rate increased by more than a factor of 10. Above 60% N_2 , the electron density rises rapidly to the pure N_2 plasma electron density which is more than three times that of pure BCl_3 . The dc bias also increased with an increase in N_2 up to 80% N_2 , then decreased for pure N_2 . The combined effect of the increase of electron density and the increase in dc bias is not likely to be sufficient to account for the magnitude of etch rate enhancement observed. Fleddermann and Hebner reported that the electron density in their

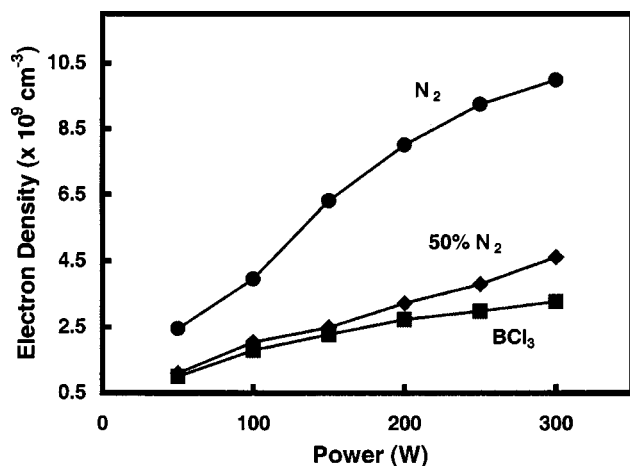


FIG. 4. Average electron density as a function of the applied rf power for N_2 , 50% N_2 in BCl_3 , and BCl_3 plasmas (15 mTorr, 20 sccm).

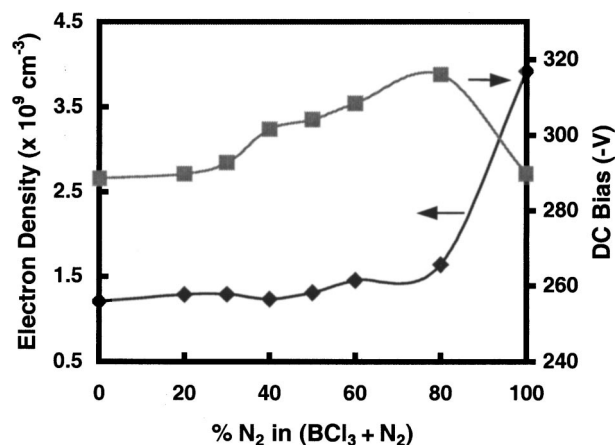


FIG. 5. Average electron density as a function of the percentage of N_2 in BCl_3/N_2 plasmas (15 mTorr, 20 sccm, 100 W).

ICP system did not change as nitrogen was added to BCl_3 , but the negative atomic chlorine ion (Cl^-) density doubled.¹⁰ It is plausible that electron attachment heating might be responsible for an increase in the production of etch species.

The QMS intensities of BCl_2 , BCl , Cl_2 , and Cl as a function of the percentage of N_2 in the flow are shown in Fig. 6. The rf power, pressure, and total flow rate were held constant at 100 W, 50 mTorr, and 20 sccm, respectively. No mass signal was detected for BN. The Cl_2 intensity increased to three times its value for pure BCl_3 at approximately 80% N_2 , and the Cl intensity decreased but exhibited a local maximum at 80% N_2 . Recombination of Cl to form Cl_2 during transport to the mass spectrometer most likely accounts for the low Cl intensity. The difference in the percentage of N_2 where the maximum etch rate occurs (15 mTorr) and the molecular chlorine mass signal peaks (50 mTorr) is probably due to the increase in pressure which was necessary to have adequate mass signals. In fact, Fedison *et al.* ob-

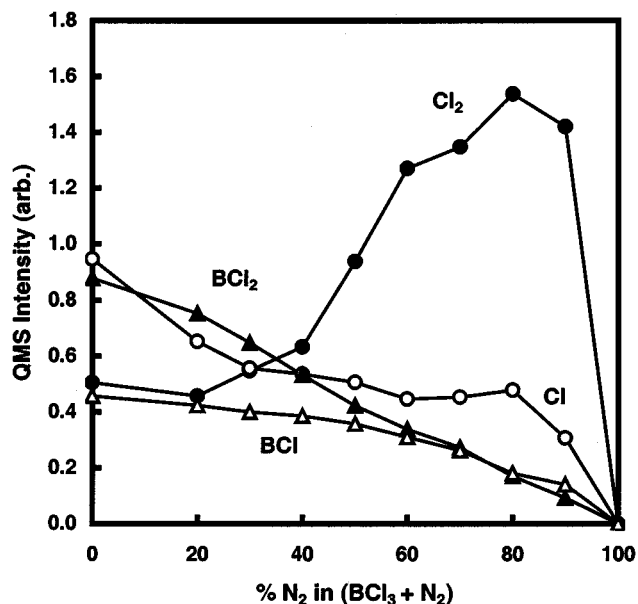


FIG. 6. QMS intensities of BCl_2 , BCl , Cl_2 , and Cl as a function of the percentage of N_2 in BCl_3/N_2 plasmas (100 W, 50 mTorr, 20 sccm).

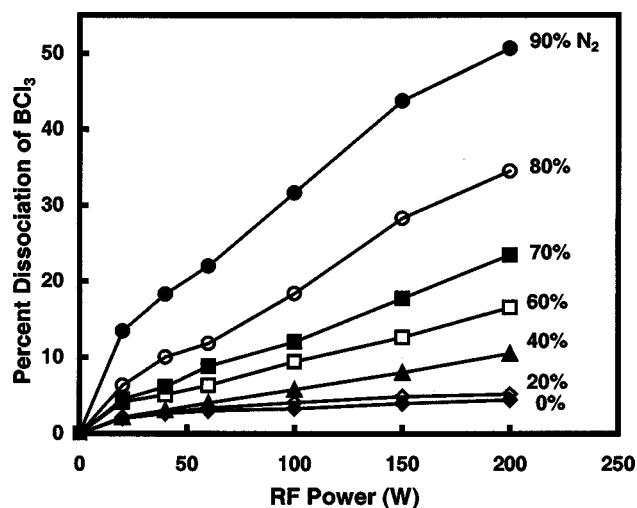


FIG. 7. Dissociation of BCl_3 as a function of the applied rf power with the percentage of N_2 as a parameter in BCl_3/N_2 plasmas (50 mTorr, 20 sccm).

served that the maximum GaN etch rate shifted toward higher N_2 percentages as the pressure was increased.⁵

The dissociation of BCl_3 was measured as a function of the applied rf power with the percentage of N_2 as a parameter and the results are shown in Fig. 7. The pressure of the system was held constant at 50 mTorr and the flow rate was maintained at 20 sccm. The dissociation of BCl_3 is defined as the difference in QMS intensity of the BCl_3 signal with the plasma on and off, divided by the intensity while off. The dissociation of BCl_3 increased with an increase in rf power regardless of the percentage of N_2 in the flow. This is consistent with the fact that higher rf power results in higher electron densities, which should enhance the dissociation of BCl_3 . For the 0% N_2 curve, the dissociation of BCl_3 is very low and shows only a slight increase with an increase in rf power. Even at a rf power of 200 W, the dissociation of pure BCl_3 was only 4.4%, which explains the very low etch observed in Fig. 1. For constant rf power, the dissociation of BCl_3 increased dramatically with an increase in the percentage of N_2 . At 90% N_2 and power of 200 W, the dissociation of BCl_3 was almost 50%.

IV. SUMMARY

The etch rate of GaAs increases dramatically with the addition of nitrogen to BCl_3 plasmas. Mass spectrometric analysis indicates that the etch rate enhancement is due to an increase in the dissociation of BCl_3 , and a subsequent increase in the production of etch species. Although the average electron density and dc bias voltage increase slightly with an increase in the percentage of nitrogen, it is unlikely that they alone account for the increase in etch rate. Optical emission from an argon actinometer increased significantly, and electron density measurements indicated that electron attachment occurred. These results suggest that an increase in the electron temperature as a result of electron attachment heating (and possibly energy transfer from N_2 metastables) is responsible for the increased dissociation and enhanced production of etch species.

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